MTE-15

Synthesis and Characterization of Mesoporous SBA-15 : A Material Evaluation for Roles in Catalysis

Ahmad Zuhairi Abdullah*, Hamidah Abdullah, Mohamad Zailani Abu Bakar, Subhash Bhatia

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia.
Tel: +604-594 1012 Fax: +604-599 6411 Email: chzuhairi@eng.usm.my

Abstract

Mesoporous molecular sieve is a new class of materials that shows high potential in various applications, particularly catalysis. A series of mesoporous materials (SBA-15) were synthesized at different gel compositions using triblock copolymer (TCP) poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) as the surfactant. Gel compositions were varied to study the effect of acidity, the contents of tetraethyl orthosilicate (TEOS) and triblock copolymer(TCP) on the characteristics of the final material. Effect of synthesis temperature was also studied. Attributed to accelerated hydrolysis of TEOS, increasing acid content in the synthesis gel favored the formation of mesopores. The best material with total surface area of 760 m^2/g, mostly in mesoporous size range was obtained at a gel composition of 1.0(TEOS):0.017(TCP):7.3HCl:115.7H_2O.The controlling mechanisms for mesopores formation were predominately influenced by the right balance between the content of TEOS and TCP in the synthesis gel that appeared to be occurring in a very narrow range. All these materials showed low crystallinity as well as weak acidity, contributed by silanol groups terminating the Si-O-Si network.

Keywords: SBA-15, Mesoporous, Catalyst, Synthesis, Characteristics.

Introduction

Despite successful application in many industrial processes, microporous materials such as zeolites become inadequate when reactants with sizes above the dimensions of the micropores (>1 nm) have to be processed [1,2]. Thus, mesoporous molecular sieves (MMSs) have introduced a new degree of freedom in the conception of catalysts. MMSs are very high surface area materials (up to 1600 m^2/g) having monodispersed pore diameters in the range 2-50 nm and a stereoregular arrangement of these channels [3]. Because of the size of their pores, they allow the processing of large molecules and the eventual accommodation of bulky intermediate transition states. This capability enables them to form catalysts or acting as catalytic supports in a wider range of industrial reactions. However, the basic understanding of the synthesis conditions is indispensable as mesoporous materials with desirable characteristics can only be obtained with properly controlled synthesis procedures [1,3]. Therefore, more research work is demanded to properly synthesize and subsequently manipulate the characteristics of these highly ordered materials towards their widest future potential applications in industrial processes [4].

Among the earliest MMSs developed are the M41S family that includes hexagonal MCM-41, cubic MCM-48 and lamellar MCM-50. Their preparation involves ionic structure directing agents and occurs via liquid-crystal templating (LCT) mechanism. These materials have uniform pores which pore sizes can be tailored in the range of 16-100Å by changing the length of the alkyl chain of the surfactant, auxiliary chemicals and reaction conditions used in their synthesis [2]. However, the main drawback for successful application of M41S is its low thermal and hydrothermal stability [1,5]. Recently, mesoporous materials with larger pore size and better stability were synthesized with the template of nonionic block copolymers. These materials, exemplified by hexagonal (*p6mm*) SBA-15, have long range order, large monodispersed mesopores (up to 50 nm) and thicker walls (typically between 3 and 9 nm) which make them more thermally and hydrothermally stable than previous materials [5, 6]. The cubic phase mesoporous material SBA-16 (*Im 3m*) possesses three-dimensional channel system and uniform-sized pore of super large cage-like structure with a cubic symmetry [7,8]. The composition of the gel and the synthesis conditions are found to strongly determine the quality of the finished SBA-15 or SBA-16 [5,6]. By focusing on the SBA-15, the in-depth understanding of the correlation between synthesis conditions with the quality of the material obtained was investigated in this study towards designing a suitable material for catalytic purposes.

Approach and Methods

Synthesis of SBA-15

The siliceous SBA-15 mesoporous materials (MM) were synthesized using tetraethyl orthosilicate (TEOS) (Merck)

as silica source, a triblock co-polymer (TCP) i.e. poly(ethylene glycol)-(propylene glycol)-poly(ethylene glycol) (Aldrich) with a molecular weight of 5800 as the structure directing agent, HCl and water. The gel's molar compositions are given in Table 1. In a typical synthesis

Table 1 Gel compositions and temperatures used in the synthesis of SBA-15 samples.

No	TEOS (g)	TCP (g)	HCl (g)	H_2O (g)	T (°C)	Molar ratio
1	24.0	11.5	21.9	300.0	60	1.0(TEOS):0.017(TCP):5.2HCl:144.7H_2O
2	24.0	11.5	26.4	270.0	60	1.0(TEOS):0.017(TCP):6.3HCl:130.2H_2O
3	24.0	11.5	30.7	240.0	60	1.0(TEOS):0.017(TCP):7.3HCl:115.7H_2O
4	18.0	11.5	26.4	270.0	60	1.0(TEOS):0.023(TCP):8.3HCl:173.6H_2O
5	30.0	11.5	26.4	270.0	60	1.0(TEOS):0.014(TCP):5.0HCl:104.2H_2O
6	24.0	7.5	26.4	270.0	60	1.0(TEOS):0.011(TCP):6.3HCl:130.2H_2O
7	24.0	15.5	26.4	270.0	60	1.0(TEOS):0.023(TCP):6.3HCl:130.2H_2O
8	24.0	11.5	26.4	270.0	40	1.0(TEOS):0.017(TCP):6.3HCl:130.2H_2O
9	24.0	11.5	26.4	270.0	50	1.0(TEOS):0.017(TCP):6.3HCl:130.2H_2O

procedure, the TCP was first dissolved in a solution of water and HCl and the mixture was shaken in an orbital shaker at 30°C and 150 rpm for 2 h. Then, the required amount of TEOS was added to the above solution. As the gel started to develop, the mixture was quickly heated to desired temperatures (T) under shaking at 75 rpm for 24 h. The gel formed was then aged at 100°C for 6 h. The solid formed was then vacuum filtered, washed several times and calcined at 500°C for 6 h in a furnace. The mesoporous materials obtained were denoted as S-1 to S-9.

Characterization of SBA-15

All SBA-15 samples were characterized for surface characteristics using a Quantachrome Autosorb-1 equipment with an outgassing temperature of 300°C. while X-ray diffraction patterns were obtained using a Siemens 2000X system. The acidity determination was made through a temperature programmed desorption of ammonia experiments using a Quantachrome Chembet 3000 system. In this test, the adsorption of NH_3 was carried out at 50°C. The Infrared spectroscopy characterization of the catalyst sample was carried out using a Perkin Elmer 2000 FT-IR system while the structure of the samples was also characterized using a Phillips CM 12 transmission electron microscope.

Results and Discussion

Surface characteristics of SBA-15

The surface area and pore characteristics of the nine SBA-15 samples produced in this study are summarized in Table 1. Bearing in mind the HCl acid content of the gel increased from S-1, S-2 to S-3, the total surface area was found to show corresponding increase. These surface areas were primarily contributed by mesopores that constituted between 62 to 73 % of the total surface area, depending on sample. The largest mesopore was demonstrated by S-3 with an average size of 6.92 nm. As a general trend in these three samples, more mesopores resulted in an increase in the pore volume. The highest pore volume was demonstrated by S-3 with a value of 0.98 cc/g. This value occurred in the normal pore volume range for SBA-15 as reported in literatures [2,4,5]. However, there was no clear correlation between the average pore width and the pore volume as they were strongly dependent on the distribution of micropores and mesopores in the sample.

The content of TEOS in the synthesis gel was increased sequentially in the preparation of S-4, S-2 and S-5 while maintaining the content of other components. Data in Table 1 suggest that with an increase in TEOS from S-4 to S-2, more mesopores formed in the SBA-15 sample. However, further increase resulted in a detrimental effect on pore formation. The decrease in the surface area and pore volume were quite drastic, suggesting the failure in the formation of mesopores in the samples at high TEOS concentration. This result suggested that in the synthesis of SBA-15, the content of the TEOS need to be neatly controlled to ensure the development of mesopores in the material. It is also noted that the average pore width failed to correlate with the formation of mesopores in the samples, suggesting the roles of macropores in between SiO_2 particles on the result of average pore widths measurement. During the synthesis, the content of TCP in the gel was increased sequentially in the preparation of S-6, S 2 and S-7 while the proportion of other gel components fixed. With an increase in the TCP content in the preparation of S-2 compared to that of in the preparation of S-6, more mesopores developed, indicated by higher total surface area and mesopore area of the latter. However, further increase in the concentration of TCP resulted in severe failure in the development of mesopores. This conclusion was based on the characteristics of S-7 which showed little porosity with low surface area. The large value of the average pore width of this sample (6.88 Å) was therefore attributable to macropores of the SiO_2 particles which had little contribution to the total surface area.

S-8, S-9 and S-2 samples were synthesized with a gelling stage conducted at a temperature of 40°C, 50°C and 60°C, respectively. It is evident in Table 2 that mesopores did not satisfactorily form at low temperatures (40°C, 50°C) as S-8 and S-9 were characterized by lower surface area and lower pore volume as compared to S-2. However, the main contributor for surface area for the former two samples was

still the mesopores that stood at between 54 to 61 % of the total surface area. This result suggested that at 40° and 50°C, synthesis of the orthosilane and the condensation of silica still can take place, although at lower rates. With an increase in temperature of the gelling stage, more ordered mesopores developed as clearly indicated by higher surface area and pore volume in the order of S-8, S-9 and S-2.

Table 2-Surface characteristics of the SBA-15 samples.

Sample	[a]Total surface area (m^2/g)	[b]Micropore area (m^2/g)	[b]Mesopore area (m^2/g)	[c]Average pore width (nm)	[d]Pore volume (cc/g)
S-1	580	205	375	6.09	0.65
S-2	606	230	376	5.87	0.92
S-3	760	208	552	6.92	0.98
S-4	324	192	132	6.73	0.36
S-5	239	84	155	6.21	0.31
S-6	503	261	242	5.45	0.74
S-7	102	63	39	6.88	0.12
S-8	371	189	202	5.47	0.43
S-9	374	143	230	6.28	0.53

[a]BET method, [b]t-method, [c]DR method, [d]MP method

Data in Table 2 suggested that among all the synthesis conditions studied, the content of TEOS and TCP in the synthesis gel were proven to more critical in the development of mesopores of the SBA-15. Despite the important roles in the successful synthesis of this mesoporous silica, the effect of content of HCl and gelling temperature in the range employed in this study was not that severe. Thus, controlling mechanisms for mesopores formation were predominately influenced by the right balance between the content of TEOS and TCP in the synthesis gel that appeared to be occurring in a very narrow range.

TEM study of the mesopores formed

Figures 1(a)-1(d) show different characteristics of mesopores formed in SBA-15 samples synthesized in this study. Generally, S-3 showed a relatively ordered mesopores, characterized by an array of straight and uniform sized pores as can be seen in Figure 1(a). The well formed mesopores correlated well with the high surface area and pore volume of this sample as indicated by data in Table 2. At low TCP content of the synthesis gel, mesopores also formed, but of less ordered manner as seen in Figure 1(b) for S-6. Meanwhile, at high TEOS content of the synthesis gel in the synthesis of S-5, satisfactory formation of mesopores also failed to occur as suggested by Figure 1(c). In Figure 1(d), it is noted that mesopores also failed to occur when the TCP content of the synthesis gel was beyond the critical limit for the formation of micelles.

XRD study of SBA-15 samples

The XRD patterns for different SBA-15 samples are shown in Figure 2. Generally, all samples were of amorphous or low crystallinity materials. Especially in samples S-1, S-2 and S-3, strong (100) peak (2θ between 1.8-1.9°), and very weak (110) (2θ between 2.4-2.5°) and (200) (2θ between 3.1-3.4°) signals were demonstrated, suggesting a high degree of hexagonal mesoscopic organization. S-3 showed the highest crystallinity among all samples synthesized in this study with an extra (210) signal occurring at 2θ=5.3°. No scattering signal was detectable for S-7, indicating this sample was of almost complete amorphous material. Samples S-4, S-5, S-8 and S-9 only exhibit very weak (100) diffraction peak that indicated the formation of poorly ordered mesoporous materials.

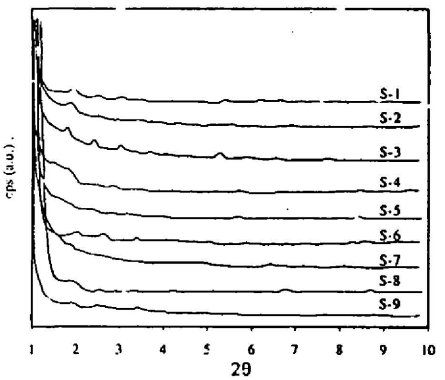

Figure 2-XRD-patterns of SBA-15 samples.

Acidity study of SBA-15

All SBA-15 samples showed single and almost symmetrical desorption peak with low acidity as suggested by small desorption peak area (0.006-0.009 mmol NH_3/g) (Figure 3). Generally, the desorption started at as early as 70°C and peaked at temperatures below 110°C. This low temperature desorption suggested that the acidity in the SBA-15 was mainly contributed by weak acid sites. The single desorption peak in Figure 3 suggested that only one type of acid sites presented in all the samples. Many researchers attributed the acidity of SBA-15 to primarily the silanol groups (Si-OH) terminating the Si-O-Si network [3,4,6,7]. In the present study, the presence of silanol groups was confirmed by an infrared absorption peak at a wave number of 3,735 cm^{-1}, especially for S-1, S-2 and S-3. It s also noted that SBA-15 samples with relatively more mesopores such as S-1-S-2, S-3 and S-6 showed both shifted desorption peaks towards higher temperature and larger peak area. These observations indicated that more silanol groups presented in these samples, positively correlating

the number of silanol groups and the occurrence of mesopores in the sample.

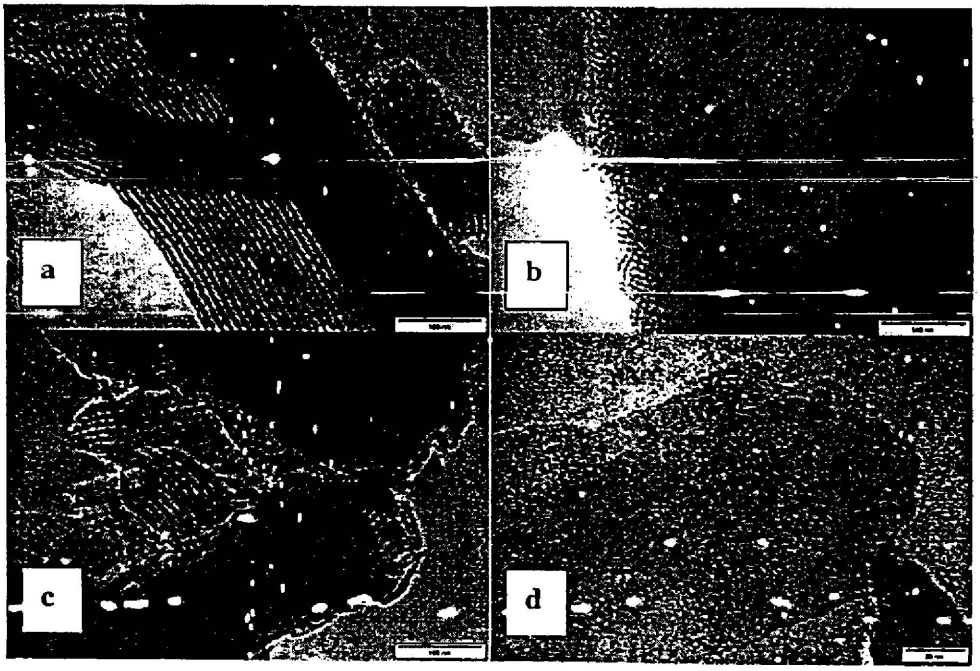

Figure 1-Different types of SBA-15 structures typically exemplified by (a) S-3 for ordered mesopores, (b) S-6 for randomly ordered mesopores, (c) S-5 for partially developed mesopores and (d) S-7 for undeveloped mesopores.

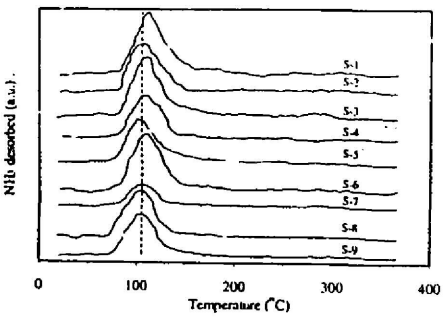

Figure 3-NH_3-TPD profiles of SBA-15 samples.

Conclusions

A series of mesoporous materials (SBA-15) were synthesized at different gel compositions using triblock copolymer (TCP) poly(ethylene glycol)-poly(propylene glycol)-poly(ethylene glycol) as the surfactant. Attributed to accelerated hydrolysis of TEOS, increasing acid content in the synthesis gel favored the formation of mesopores. The best material with total surface area of 760 m^2/g, mostly in mesoporous size range was obtained at a gel composition of 1.0(TEOS):0.017(TCP):7.3HCl:115.7H_2O.The controlling mechanisms for mesopores formation were predominately influenced by the right balance between the content of TEOS and TCP in the synthesis gel that appeared to be occurring in a very narrow range. Successful development of SBA-15 resulted in a material with well ordered and straight array of pores of meso size range. All these materials showed low crystallinity as well as weak acidity, contributed by silanol groups terminating the Si-O-Si network.

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